

STUDIES ON THE STABILITY AND SEDIMENT PRECURSORS IN VISBREAKER MIDDLE DISTILLATE

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ABSTRACT

Diesel fuels, particularly those incorporating secondary processed stocks, can degrade during long term storage. The degradation products can cause plugging of fuel filters and blockage of engine components. In the present paper, stability of a middle distillate cut of visbroken product from a refinery unit, before and after extraction with methanol under ambient storage conditions, has been determined. Methanol extraction has been found to reduce the tendency of the fuel to form insolubles significantly and it also separates out sediment precursors. The sediment precursors responsible for the instability of the fuel obtained under different conditions of extraction were characterized for their functional groups by FTIR. Effect of blending the sediment precursors into a typical feed stock on the stability under accelerated aging has also been studied.

INTRODUCTION

Visbreaking is not only used for reducing the viscosity and pour point of heavy fuel oils and residues but also produces relatively cleaner feed stocks for catalytic cracking units. Middle distillates from visbreakers are blended with diesel pool, which enhances the stability problem. Recently Wechter & Hardy¹ and Sharma & Agrawal²⁻³ have reported that methanol extraction removes the major portion of sediment precursors in case of light cycle oil (LCO) and total cycle oil (TCO). The present paper reports the stability behaviour of a visbreaker middle distillate from a refinery stream and the effect of methanol extraction, particularly fuel to methanol ratio on the removal of sediment precursors. These sediment precursors have also been characterized using FTIR technique and the effect of different doses of total sediment precursors on sediment formation determined.

EXPERIMENTAL

The storage stability of the visbreaker middle distillate fuel was determined in terms of total insolubles after keeping it for 3,6, and 9 months under ambient conditions. Sediment (insoluble) precursors were separated from the fuel using methanol in sample to solvent ratio 5:1, 5:3, 5:5 and 5:10 by vol, till a neutral (stable) fuel is obtained. The fuel solvent mixture was shaken manually for 10 minutes and was kept over night for separating the fuel and solvent layer. Methanol was recovered from the upper layer by distillation to get the insolubles / sediment precursors (SP1, SP2, SP3 and SP4) as residue. Figure-1 presents the scheme employed for the above extraction.

These residues were characterized by FTIR as thin films obtained from evaporating their solutions in dichloromethane on KBr plates. Different fuels obtained after removing the sediment precursors during consequent extraction were stored under ambient conditions for 7 months and total insolubles were determined. Total sediment precursors SP (SP1+SP2+SP3+SP4) were doped in stable fuel(F4) in different concentrations and their stability was determined by modified UOP-413 accelerated test method (100 psi pressure of oxygen, 4 hours, 100 °C). Physico-chemical properties of visbreaker middle distillate and total sediment precursors were determined using standard IP/ASTM methods.

RESULTS AND DISCUSSION

The physico-chemical properties of fuel and total sediment precursors are

reported in Table- 1 while total insolubles yield under ambient storage conditions are presented in Figure-2. Physico-chemical data of visbroken middle distillate (Table 1) reveals that the fuel is quite unstable due to presence of higher bromine number, sulphur and nitrogen content (more than 50% of nitrogen basic in nature). This trend is supported from the insoluble yield obtained from this fuel under ambient storage for different time intervals, which shows an increasing trend (Figure-2) upto 9months (maximum storage time in the present study).

The elemental composition of total sediment precursors indicate that nitrogen and sulphur containing aromatic structures are predominantly responsible for sediment formation. This is supported by H/C atomic ratio (1.36 as compared to 1.63 in fuel).

Figure-1 shows that the sediment precursors yield is increasing with decreasing fuel to solvent ratio (F/S). It has been observed that with F/S 5:10 ratio (at fourth stage) most of the precursors are extracted out and the fuel becomes practically stable during ambient storage of seven months. This has been confirmed by keeping the fuels (F,F1,F2,F3, and F4) for seven months under ambient storage conditions and determining the yield of insolubles .Total insolubles obtained from different fuel (F1,F2,F3, and F4) under ambient storage of seven months are shown in Figure-3. It has been observed (Figure-3) that total insolubles decreases slowly in F1, F2, and F3, while in F4 the decrease is quite significant and fuel becomes practically stable.

This fuel (F4) has further been doped with different concentrations (1, 3 and 5 % wt/vol) of total sediment precursors (SP) and stability determined by modified UOP-413 accelerated test method. The results obtained are presented in Figure.4, which reveal that the sediment yield increases with increase of sediment precursors added. Further, it is also observed from the Figure-4 that the added precursors are more effective in sediment formation compared to those present in the original fuel.

The FTIR spectra of different precursors (SP1, SP2, SP3 and SP4) are mainly of same nature. The bands at 749, 811 and 875 cm^{-1} (with decreasing relative intensity) are observed in all the precursors, showing the same type of substitution pattern on aromatic ring . The broad OH/NH stretching bands around 3300 cm^{-1} and broad carbonyl band at around 1700 cm^{-1} are found to decrease in intensity from SP1 to SP4. The absence of band at 720 cm^{-1} (due to n-paraffinic $(\text{CH}_2)_n$, $n \geq 4$) and relatively stronger band at 1456 cm^{-1} due to $-\text{CH}_2$ bending indicates the presence of significant concentrations of naphthenic structures in all the precursors.

The study thus indicated that repeated methanol extractions are required for getting the stable fuel from visbreaker middle distillate product.

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TABLE- 1 Characteristics of visbreaker middle distillate and total sediment precursors

Visbreaker Middle Distillates		Total Sediment precursors (SP)	
Density, D15	0.8617	C, % Wt	85.40
Bromine number	20.7	H, % Wt	9.65
Nitrogen Total, ppm	237.3	S, % Wt	3.46
Sulfur Total,% wt	1.65	N, % Wt	0.36
Nitrogen Basic, ppm	138	O, % Wt	1.23
Carbon residue, %wt	0.04	Nitrogen Basic, ppm	932
C,% wt	83.95	Molecular Weight	274
H,% wt	11.40	Atomic H/C ratio	1.36
Atomic H/C ratio	1.63		
Molecular weight	255		
Boiling range, °C	176-393		

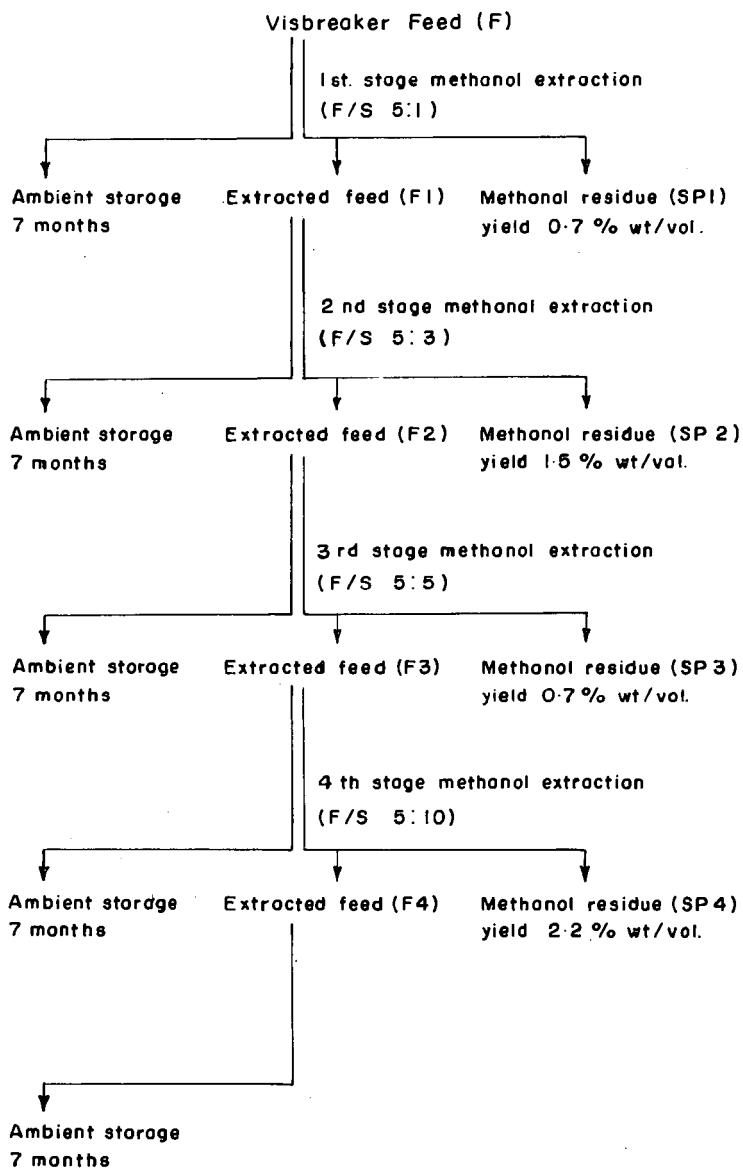


Fig. 1 - Scheme used for the extraction of insolubles / sediment precursors.

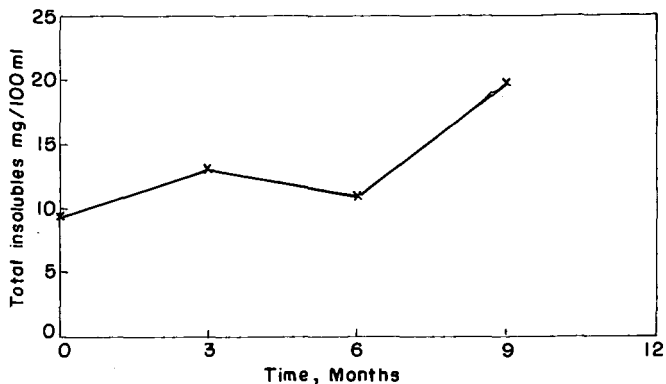
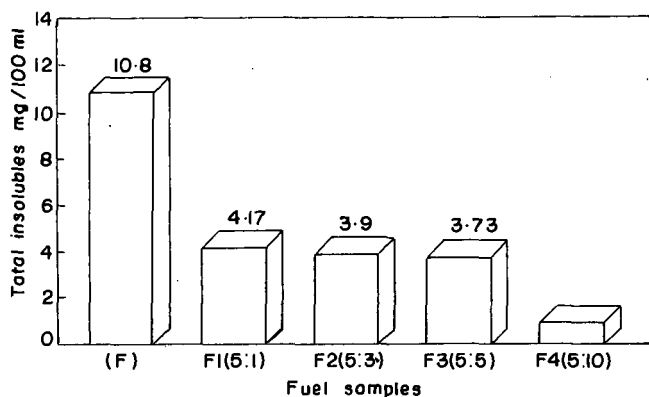


Fig. 2- Total insolubles Vs time during ambient storage stability of visbroken middle distillate.



(Feed to Methanol ratio given in brackets)

Fig. 3- Effect of extraction on ambient storage stability (7 months) of visbroken middle distillate.

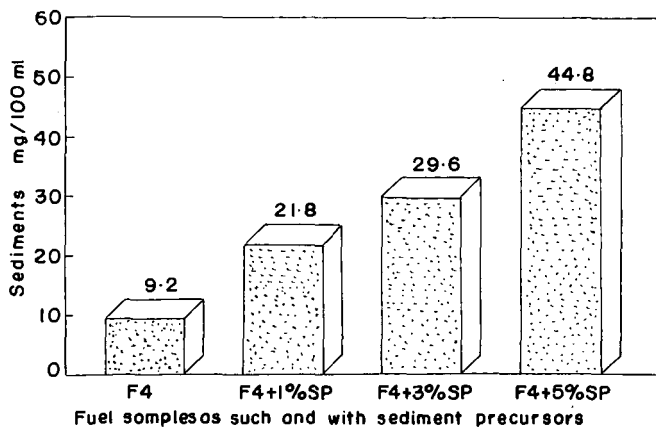


Fig. 4- Effect of sediment precursors on extracted visbroken middle distillate (UOP-413 MODIFIED)